PREFACE

Among the natural products, terpenoids holds special appeal to synthetic organic chemists, as they provide fertile ground for developing and testing new methodologies, because of the phenomenal structural diversity present in them. The present thesis entitled "Synthesis of 6-epijunicedranol; Spirocyclopentannulation strategies; and Exploratory studies towards chiral taxanes" describes the first total synthesis of a junicedrane; development of two methodologies for the spiroannulation of cyclopentenones and a new strategy for chiral taxanes starting from R-carvone. For the convenience, the results are presented in three chapters; viz (1) First total synthesis of a junicedrane; (2) Approaches to spiroannulation of cyclopentenones. Formal total synthesis of acorones; and (3) Exploratory studies towards chiral taxanes. In all the chapters, the compounds are sequentially numbered (bold), and references are marked sequentially as superscripts and listed at the end of each chapter. All the figures included in this thesis were obtained by ***direct xerox*** *of the original NMR spectra, and in some of them uninformative areas have been cut to save the space. In the experimental section, for some of the compounds in third chapter, nonsystematic names were used to maintain the atom numbering in the series.*

The first total synthesis of a junicedrane, member of a new tricyclic sesquiterpene group containing four contiguous quaternary carbon atoms has been described in the first chapter of the thesis. Thus, the first total synthesis of (±)-6-epijunicedranol, an epimer of the natural product junicedranol, was achieved starting from the readily available cyclogeraniol employing a biogenetically patterned acid catalysed carbonium ion mediated cyclisation and rearrangement of a dienone as the key step. One pot Claisen rearrangement of cyclogeraniol using ethyl vinyl ether in the presensce of a catalytic amount of mercuric acetate furnished an aldehyde, which was transformed into the key intermediate of the sequence, a dienone via Grignard reaction-oxidation protocol. Rearrangement of the dienone with a catalytic amount of borontrifluoride etherate furnished (±)-6-epijunicedranone, in which four contiguous quaternary carbon atoms were efficiently generated.

Development of two methodologies for the spiroannulation of cyclopentenones and extension to the formal total synthesis of the spirosesquiterpenes acorones is described in the second chapter of the thesis. The first method was based on Claisen rearrangement-Wacker oxidation and intramolecular aldol condensation strategy leading to spiro[4.n](n+5)alk-2-en-

1-ones starting from cyclic ketones. The second spiroannulation methodology was based on Claisen rearrangement-ozonolysis-intramolecular aldol condensation strategy leading to spiro[4.n](n+5)alk-3-en-2-ones from cyclic ketones. As an application to the second methodology, formal total synthesis of acorone and isoacorones has been accomplished starting from cyclohexane-1,4-dione.

A new approach to chiral A-ring derivatives and B-secoderivatives of taxanes starting from the readily available monoterpene R-carvone is described in the third chapter of the thesis. To begin with, R-carvone was converted into two A-ring derivatives of taxanes by employing an alkylative 1,3-enone transposition, Wacker oxidation and ozonolysis sequence. It was then extended to the synthesis of chiral A-ring derivatives of taxanes those are suitable for further elaboration. A few unsuccessful attempts were made for the construction of the AB ring system of taxanes via the formation of C-3, C-8; C-2, C-3; C-8, C-9; and C-9, C-10 bonds employing intramolecular aldol condensation; ene reaction; 1,6-Michael addition, radical cyclisation; ring closing metathesis based strategies. Construction of A-ring derivatives was further extended to the synthesis of 19,20-bisnor-(2,3)-seco-C-aromatic taxane derivativess. In another direction R-carvone was also elaborated into the C-ring derivatives of taxanes employing a 5-exo-trig radical cyclisation as key reaction. Finally, carvone and 6,6-dimethylcarvones were linked through an acetylene to generate a derivative of B-secotaxane, 13-tert-butyldimethylsilyloxy-1,6-diisopropenyl-19,20-bisnor-(1,2)-seco-taxa-3(8),11-dien-4-one.